



Hierarchical porosity and electrolyte compatibility in carbon-based supercapacitors: Structure-performance relationship

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HIGHLIGHTS

- Hierarchical slit-pores are key for high supercapacitor performance.
- Quasi-elastic neutron scattering reveals confined ion dynamics.
- Charge storage can be decoupled from long-range ion diffusion.
- A hybrid capacitive-pseudocapacitive storage mechanism is proven.
- Pore geometry dictates electrolyte compatibility and energy density.

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ABSTRACT

Supercapacitors are pivotal for high-power energy storage, yet their energy density is governed by the complex interplay between electrode porosity and electrolyte properties. This study reveals how hierarchical porosity dictates the electrochemical performance of carbon-based electrodes—activated carbon from coconut shell (ACMag), commercial activated carbon (ACNag), and reduced graphene oxide (rGOag)—in aqueous (KOH) and deep eutectic solvent (ChClEG) electrolytes. We demonstrate that ACNag, with its hierarchical slit-shaped pores, delivers superior and stable performance (34F/g, 15.6 Ω cm² in ChClEG). Conversely, ACMag's "ink-bottle" pores cause ion-trapping and higher resistance, while rGOag exhibits extreme electrolyte dependence, excelling in KOH (68 F/g) but failing in viscous ChClEG (8 F/g) due to inadequate porosity. By integrating electrochemical, structural (BET, SEM), and chemical (TG-FTIR-MS) analyses, we establish that optimal capacitance arises from a synergy of electric double-layer formation and surface-mediated pseudocapacitance. Quasi-elastic neutron scattering further shows efficient charge storage occurs via rapid ion diffusion or localized, surface-confined processes. Our findings prove that tailoring hierarchical slit-pores is paramount for balancing ion confinement and accessibility, providing a critical design principle for advanced supercapacitors in renewable energy and high-power applications.

1. Introduction

Supercapacitors (SCs) are increasingly recognized as efficient energy storage devices due to their rapid charge/discharge rates, extended cycle stability, and high specific power [1,2]. Because of this, a critical

area of research focuses on identifying cost-effective electrode materials with high surface area, thermal stability, conductivity, porosity, and low production costs [3,4]. Consequently, carbon-based materials, including activated carbon (AC) and graphene, have emerged as leading choices for SC electrodes due to their abundance, high chemical stability, and

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excellent conductivity [5–7]. Even if AC is typically derived from precursors such as coal, peat, and lignite, alternative sources like agricultural residues are more and more investigated [8,9]. Notably, the Macaúba endocarp, *Acrocomia aculeata* species, abundant in South America, presents an appealing option due to its high lignin and carbon content [10–15]. Another promising electrode material is reduced graphene oxide (rGO). Here improved electrical properties are enabled by the HDDR (hydrogenation, disproportionation, desorption, and recombination) process [16–18].

Since SC energy storage relies on electrostatic ion adsorption at the electrode–electrolyte interface (EEI), forming the electric double layer (EDL), the pore structure of the electrodes materials, specifically the distribution of micropores (< 2 nm) and mesopores (2 – 50 nm), critically affects ion migration and EDL formation [19,20]. This means that the surface area and pore architecture need to be controlled [21,22]. Besides, the electrolytes, essential to cell resistance and operating potential window (OPW), are selected based on factors such as ionic radius, conductivity, and chemical stability [23,24]. In this context, several types of electrolytes have been reported in literature and classified into two types: liquid electrolytes, which are divided into aqueous, organic, and ionic liquids (IL); and organic and inorganic solid or near-solid electrolytes [25]. To overcome high cost and negative environmental impact of ILs, deep eutectic solvents (DES), have become attractive due to their high purity, low cost, and, in general, low or even zero toxicity [26–28]. DES's are liquids originated from the simple mixture of two or more compounds capable of joining together, through the interaction of hydrogen bonds, in a given molar ratio, resulting in a system whose melting point is lower than that of its isolated constituents [29,30]. Deep eutectic solvents (DES), formed via hydrogen bond interactions between components, offer advantages over traditional electrolytes like aqueous KOH. DES-based electrolytes demonstrate wider operating potential windows and lower viscosity, enhancing ion transport and SC performance [31,32]. The eutectic mixture of choline chloride and ethylene glycol (1 : 2 molar ratio) provides a promising alternative, with an OPW (–0.9 to + 1.25 V) surpassing aqueous electrolytes [33]. However, aqueous KOH still offers lower resistance and higher specific power [34].

Despite their high-power density and long cycle life, the energy density of traditional carbon-based supercapacitors remains a key challenge for practical applications. Recent breakthroughs in hierarchical porous carbon-based hybrid systems, such as zinc-ion hybrid capacitors, have demonstrated remarkably high energy densities by ingeniously combining capacitive and battery-type charge storage mechanisms [35–37]. These works underscore the critical importance of tailored porosity and surface chemistry in optimizing electrolyte accessibility and facilitating fast redox reactions, providing a valuable roadmap for future performance enhancements.

Aiming to investigate the electrochemical performance of supercapacitors made using activated carbon (AC), one produced entirely from coconut shell and the other a commercial product, and a commercial reduced graphene oxide (rGO), this study compares their behavior in aqueous KOH and DES electrolytes using cyclic voltammetry (CV) and galvanostatic charge–discharge (GC). From the obtained results, it was clear that characterization of the electrode properties prior to electrolyte uptake is critical to understanding the relationship between pore structure, chemical composition, and performance. Under these lines, to determine the surface area and pore size distribution of the samples, the Brunauer–Emmett–Teller nitrogen adsorption/desorption technique (BET) was applied. This technique analyzes the adsorption of gas molecules on the surface of a material, providing key information about its porosity and textural properties. For AC, the pore structure influences ion transport and electric double-layer formation, which are essential for energy storage. In rGO, BET analysis helps assess the extent of exfoliation and porosity, which contributes to its electrochemical behavior. Thermogravimetric analysis coupled with Fourier-transform infrared spectroscopy and mass spectrometry (TG-FTIR-MS)

was used to evaluate the thermal stability and chemical transformations of the materials during heating. This technique monitors mass changes as a function of temperature and identifies the gases evolved, offering insights into the thermal decomposition and structural modifications of the analyzed material [38]. For AC, TG-FTIR-MS aids characterizing changes in its porous network, while for rGO, it reveals details about residual functional groups and thermal reduction processes.

A good understanding of EEI microscopic structure and ions dynamics is of paramount importance for optimal design of energy storage devices. Neutron spectroscopy (NS), and in particular quasi-elastic neutron scattering (QENS), is a powerful technique for studying the dynamical response of mobile atoms in materials. QENS provides insights into the average motional behavior of atoms, particularly hydrogenous species, due to its high value of total neutron scattering cross-section of 82.02 b for 25 meV-cold neutrons, of which incoherent cross-section account for 80.26 b [39]. In this study, QENS was employed to investigate the changes in hydrogen bonding interactions within the framework of activated carbon and reduced graphene oxide porous electrodes after the uptake of aqueous KOH and DES electrolytes. Specifically, an aqueous solution containing potassium hydroxide KOH and a eutectic mixture choline chloride and ethylene glycol were used.

2. Materials and methods

2.1. Electrodes and electrolytes

The electrodes were fabricated using activated carbon (AC) and commercial reduced graphene oxide (rGO). Two types of activated carbon were analyzed: one produced entirely from coconut shell sourced from Macaúba native to Paraguay (referred to as ACM) and the other a commercial product supplied by Nuclear Ltd. (referred to as ACN). The electrolytes used in this study included an aqueous solution of potassium hydroxide (KOH) and a eutectic mixture of choline chloride and ethylene glycol (ChClEG) in a 1:2 M ratio.

Obtaining activated carbon from coconut shells (ACM): To ensure clean starting materials, the coconut husk pieces were cut into smaller fragments, soaked in distilled water for 24 h, and then the water was decanted. The rinsed bagasse was dried in an oven at 120 °C for 24 h. The dried bagasse was then carbonized in a tube furnace under a nitrogen atmosphere. The furnace was heated from ambient temperature to 600 °C at a rate of 10 °C per minute and then held at that temperature for 2 h. The resulting char was then activated using steam. This process involved reheating the char to 600 °C at a rate of 10 °C/min and maintaining this temperature for 1 h under a steam flow of 0.023 ± 0.001 kg/h. After activation, the furnace was cooled to 30 °C [40–42].

Hydrogenation disproportionation desorption and recombination (HDDR) reduction: Prior to electrode production, ACM, ACN and rGO were heat treated at 400 °C using the HDDR process with 2 bar hydrogen pressure [43], ground and then passed through a 53 µm sieve.

Electrode synthesis: The electrode is defined as the agglomerate of active material (ACN, ACM, or rGO), carbon black (CB), and polytetrafluoroethylene (PTFE). Isopropyl alcohol (IPA, C₃H₈O) was selected as the diluent medium due to its efficacy in dispersing PTFE [44], optimal wetting of carbon materials, suitable volatility for easy removal during drying, and ability to ensure a homogeneous mixture free of solvent residues. The synthesis used approximately 100 mg (57 %) of ground and sieved AC (53 µm), mixed with 12.5 mg (7 %) of CB (Vulcan XC-72-R, Cabot Corporation) and 64 mg (36 %) of PTFE (with 60 % H₂O, yielding ~40 mg pure PTFE). The mixture was stirred at 40 °C until complete IPA evaporation. The resulting agglomerates were ready for characterization. For rGO-based electrodes, the same procedure was followed as described in Benítez Jara et al. (2020) [16].

Electrolyte synthesis: First, the DES electrolyte was prepared using the mixture of 1 mol of choline chloride (ChCl, 2-hydroxy-N, N, N-trimethyl-ethyl ammonium chloride, 99%) and 2 mols of ethylene glycol (EG) (1,2 ethanediol, 99.8% or C₂H₆O₂). For comparison, aqueous

electrolyte potassium hydroxide with 1 molar concentration (KOH 1M) was also used.

The following nomenclature has been adopted to describe the samples: ACMP, ACNP, and rGOP refer to the starting materials in powder form. From these materials, the electrodes (agglomerated samples = ag) were prepared and labeled as ACMag, ACNUag, and rGOag. The electrodes were then immersed in electrolytes, and the samples with electrolyte were categorized into two groups: those soaked in KOH (ACMagKOH, ACNagKOH, and rGOagKOH) and those soaked in ChClEG (ACMagChClEG, ACNagChClEG, and rGOagChClEG). Table 1 summarizes the samples and their nomenclature, as well as the techniques used to characterize them.

2.2. Material characterization methods

2.2.1. Determining the specific capacitance and ESR

The first characterization step of the electrode materials was the electrochemical behavior of the supercapacitors analyzed by cyclic voltammetry (CV) and Galvanostatic charge–discharge cycles (GC) using the Arbin BT-4 (Software MITS Pro-4) analyzer.

Table 1

Sample Types, Labels and Techniques Overview. Sample types include ACMP, ACNP, rGOP powder samples; ACMag, ACNag and rGOag referred to as laminated electrodes soaked with KOH and ChClEG electrolytes. The table is organized to distinguish between the different sample treatments and the specific techniques used in processing or evaluating the samples.

Samples	Technique	Purpose	Parameters/Details
ACMP ACNP rGOP	BET	Surface area, pore volume analysis	- N ₂ adsorption at −195.85 °C - BET equation (surface area) Dubinin-Radushkevich (DR) for micropores Total pore volume at P/P ₀ = 0.99.
	TG-FTIR-MS	Thermal stability, evolved gas analysis	- Temperature range: RT to 600 °C, 5 K/min- N ₂ flow FTIR acquisition every 3 °C Continuous MS monitoring.
ACMag-Dry ACMag-KOH ACMag-ChClEG ACNag-Dry ACNag-KOH ACNag-ChClEG rGOag-Dry rGOag-KOH rGOag-ChClEG	Neutron Spectroscopy	Study hydrogen dynamics and electrolyte behavior within electrode pores	- FOCUS cold neutron time-of-flight spectrometer - Room temperature - Incident wavelength: 6 Å - Elastic energy resolution: ~54 meV - Momentum transfer (Q): 0.35–1.55 Å ^{−1} - Relaxation times: 4.15–81.46 ps - Vanadium reference for calibration - Al sample holder coated with Nb to prevent oxidation.
ACMag-KOH/ ACNag-KOH/ rGOag-KOH/ ACMag-ChClEG/ ACNag-ChClEG/ rGOag-ChClEG	CV	Electrochemical capacitance via voltammogram integration	- Scan rates: 1–100 mV/s - Voltage range: 0–1 V - Capacitance = ∫i.dV/(2vΔV).
	GCD	Charge-discharge behavior, ESR analysis.	- Current density: 10 mA/g - Voltage range: 0–1 V - ESR = ΔV/(2I).

Cyclic Voltammetry and Galvanostatic charge–discharge cycles: CV is a commonly used technique for obtaining electrical parameters and evaluating SC performance, providing a measure of charge response of supercapacitors with respect to a time-varying (increasing and decreasing) potential and allowing for evaluating capacitance [45]. The experimental procedure consists in applying a time-varying and cyclic potential to an electrode that is immersed in an electrolyte while measuring the resulting current (response current). The correlation between applied potential and response current generates the voltammogram, which is a plot of current versus potential in which the potential direction is reversed at the end of the sweep [46].

In CV, the evaluation of the capacitance value, is based on the voltammogram area, which is integrated providing the i.V product, and then divided by the double product between the potential window and the scan rate [47]. The capacitance C can be calculated by applying equation (5):

$$C = \frac{\int_{V_0}^{V_{\max}} i(V) dV}{2v\Delta V} \quad (F) \quad (5)$$

The specific capacitance C_s is the capacitance C per unit mass and is calculated by means of equation (6).

$$C_s = \frac{4C}{M} \quad (6)$$

where, M = m₁ + m₂ is the total mass considering the mass of each electrode.

Galvanostatic charge-discharge cycling is another technique used in the characterization of SC's [48,49]. The process involves applying a fixed current to a cell in the form of constant current charge and discharge (CCCD) and recording the corresponding change in voltage as a function of time [48]. One of the key parameters that can be derived from galvanostatic charge-discharge data is the equivalent series resistance (ESR). ESR is an important factor in determining the performance of a supercapacitor. Despite its importance, there is no consensus in the literature on the determination of this parameter from galvanostatic charge-discharge data [50]. A common method for calculating ESR is to use the voltage drop (ΔV) observed at the charge-discharge transition for a given applied current (I). In equation (7), Ohm's law is then used to obtain the ESR.

$$ESR = \frac{\Delta V}{I} \quad (7)$$

However, to obtain reliable ESR values, the voltage drop must be normalized by a factor of two (e.g., ESR = ΔV/(2I) [50].

In this work, all CV experiments were carried out using scan rates from 1 mVs^{−1} to 100 mVs^{−1} with a maximum operating potential of 1 V, while the GC tests were carried out with a current density of 10 mA g^{−1} and a potential window from 0 V to 1 V.

The SCs were assembled by creating a homogeneous mixture of AC laminated with a borosilicate glass rod, which to take the shape of the current collector was disk-shaped with, a 1.4 cm diameter. Figure S 1 (in supplementary information) shows the electrodes that were glued to the current collector to form symmetrical capacitors. Electrodes were bonded using a silver conductive ink and left to dry for 1 hour at 50 °C in an oven. After drying, the electrodes were immersed in a beaker containing the electrolytes and left soaking for 24 hours.

2.2.2. Determining the chemical structure of the raw material

Brunauer-Emmett-Teller nitrogen adsorption/desorption technique: To determine surface area, automated gas adsorption analyzer, Micromeritics ASAP 2020 Surface Analyzer was used with adsorption-desorption isotherms of nitrogen at −195.85 °C (77 K). Prior to analysis, the samples were degassed at 200 °C under a dynamic vacuum. The degassing process was continued until a stable vacuum level of 1–2 μm

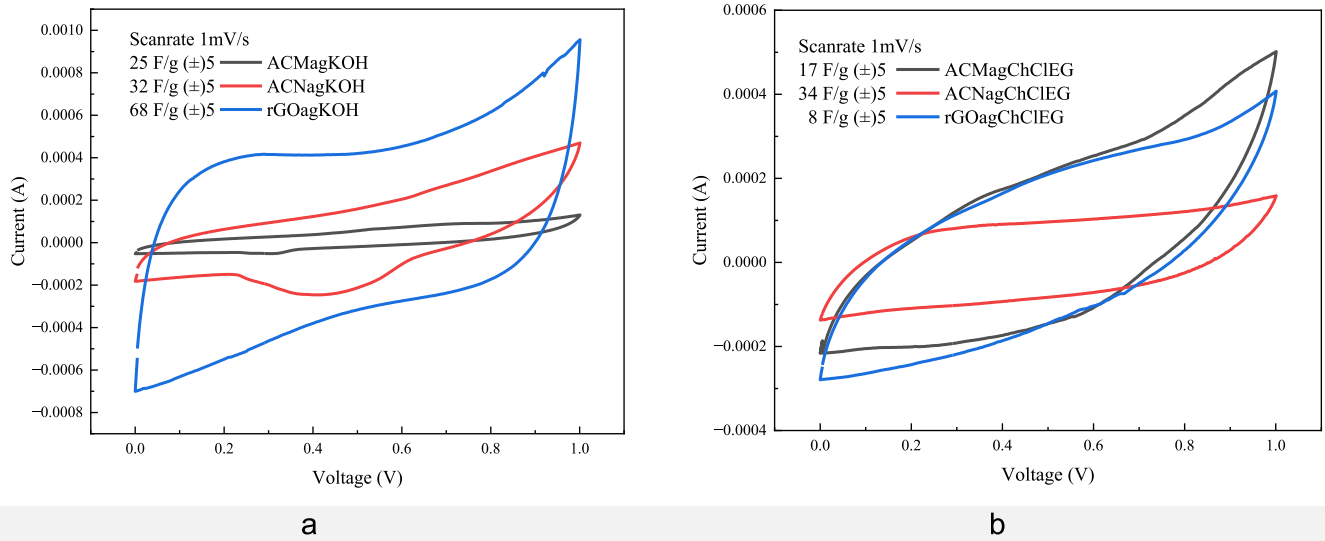


Fig. 1. Voltammograms resulting from the cyclic voltammetry of capacitors with eutectic electrolyte a) ChClEG and b) KOH.

Hg was attained, confirmed by isolating the sample tube and observing no pressure increase over time. This ensured the complete removal of surface moisture and contaminants. The specific surface areas of each sample were calculated by the BET method while volume of micropore was estimated using the Dubinin Radushkevich (DR) equation. For pore volume, it was directly calculated from the volume of nitrogen held at the highest relative pressure ($P/P_0 = 0.99$) [51].

Thermogravimetric analysis coupled to Fourier Transform infrared and Mass Spectroscopy (TGA-FTIR-MS): To get a full overview of the powdered samples chemical structure, TG-FTIR-MS measurements were performed. In this analysis, the samples were subjected to thermal degradation while recording the evolved gas by FTIR and MS. Changes in the mass of the sample as a function of temperature observed by TGA give insight into the sample decomposition, while the slope of mass loss indicates how rapidly the decomposition occurs. The gases released during the heating process for each sample are characterized by an attached FTIR and MS spectrometer to determine the nature of the decomposition products [52]. FTIR facilitates the understanding of the decomposition process [53] since the measured spectra is a unique fingerprint of the sample, with absorption peaks corresponding to the frequencies of the vibrations between the bonds of the atoms that make up the material. Additionally, the MS data allows for measuring the mass-to-charge ratio of gas-phase ions with extremely high accuracy acting as a complementary quantitative analysis of the gaseous components.

Evolved gas analysis measurements were carried out using the PERSEUS TG 209 F1 Libra (NETZSCH, Germany) coupled with a Fourier transform infrared (FTIR) spectrometer (BRUKER Optics Inc., Germany) and an Aeolos QMS403D (NETZSCH, Germany) using an automatic sample changer. Powdered and agglomerated samples were placed in open alumina crucibles and heated from room temperature (RT) to 600° C at a constant heating rate of 5 K/min under 20 ml/min of nitrogen as the protective gas and an additional 20 ml/min of N₂ as the purge gas. FTIR spectra of the evolved gases was recorded every 3° C and MS data was collected continuously during the heating process.

Neutron spectroscopy: (Quasi Elastic Neutron Scattering (QENS)): To obtain a complete picture of the electrolyte-electrolyte system and the dynamic behavior of hydrogen atoms within the electrode pores, neutron spectroscopy experiments were carried out using the FOCUS cold neutron time-of-flight spectrometer. Data were collected at room temperature with an incident neutron wavelength of 6 Å and an angle of 90° with respect to the incident neutron beam direction. This experimental setup resulted in an elastic energy resolution

of ~54 meV, an accessible momentum transfer from 0.35 to 1.55 Å⁻¹, and an energy transfer range from 0.25 to 4.97 meV, which covers the relaxation time from 81.46 to 4.15 ps. An empty cell was measured to subtract the background and to calibrate the detector using a vanadium reference. To conduct the neutron spectroscopy experiments, part of the mass of the agglomerates was taken (see section 2.1: “Electrode synthesis”). The electrodes were laminated to match the internal shape of the aluminum sample holders, as shown in Figure S 2. Subsequently immersed in each of the electrolytes and left to soak for a week. To avoid oxidation all samples were wrapped in a thin niobium film and placed inside a flat thin-walled sample holder. Samples not immersed in electrolytes (Dry) were also evaluated for comparison.

Since individual trajectories of all the distinct relaxation processes cannot be distinguished and considering that the measured signal originates from relaxation phenomena, the observed scattering signal, $S(Q, \omega)$, was modelled by the convolution of one Delta function and one Lorentzian function using eq (8).

$$S(Q, \omega) = \text{DWF}[A_0(Q)\delta(\omega) + (1 + A_0(Q)L(\Gamma, \omega))] \otimes R(Q, \omega) + B(Q) \quad (8)$$

where DWF is the Debye-Waller factor; A_0 is the incoherent scattering factor (EISF) which gives insight into the geometry of motions; and $L(\Gamma, \omega)$ indicates the Lorentzian function representing the broadening distribution that results from neutron-nucleus collisions, corresponding to the population statistics of one relaxation process. $R(Q, \omega)$ represents the resolution function of the instrument and $B(Q)$ a flat background term that also includes spectral intensity arising from fast motions outside the instrument resolution. $\delta(\omega)$ is a delta function that represents the particles that are seen as immobile in the time window probed by the spectrometer [54]. The data were analyzed using the DAVE software [55].

Based on previous work [56], here it is also assumed that between two events giving rise to diffusion, the particle remains at a given location for a time τ_0 , well before the duration of the jump τ , and in this case, the dynamical structure is written as:

$$S(Q, \omega) = \frac{1}{\pi} \frac{f(Q)}{f(Q)^2 + (\hbar\omega)^2} \quad (9)$$

$S(Q, \hbar\omega)$ is the Lorentzian line with a HWHM given by:

$$\Gamma = \frac{\hbar D_i Q^2}{1 + \hbar D_i Q^2 \tau_0} \quad (10)$$

At small Q , the Q dependence of $f(Q)$ is similar to the one of the long-

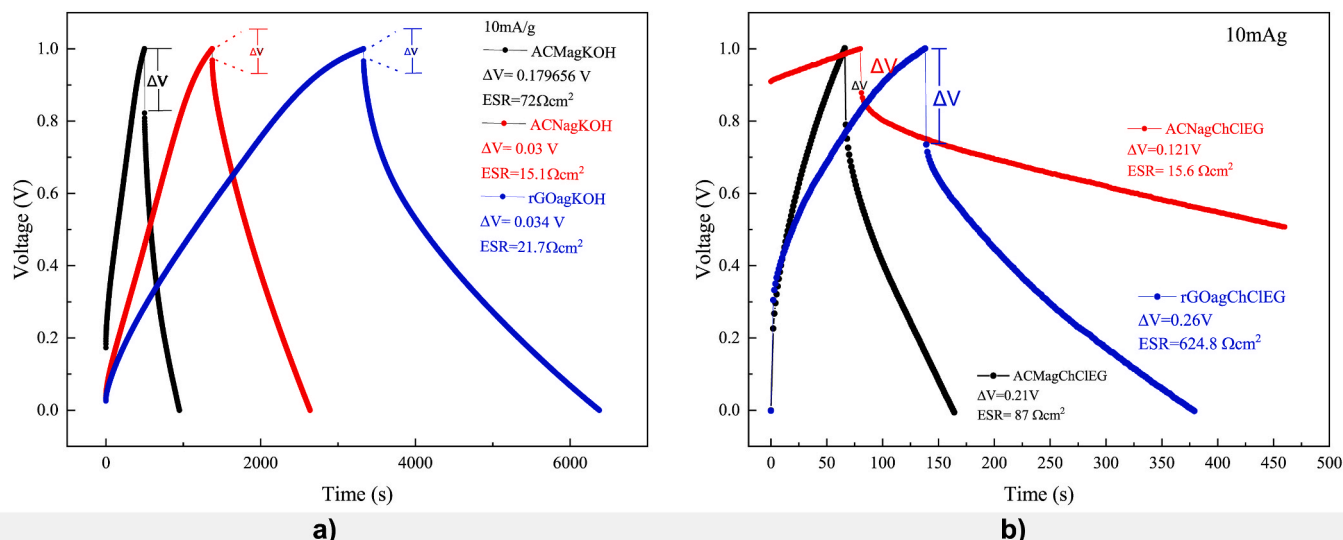


Fig. 2. GCD curves for a) aqueous KOH and b) eutectic ChClEG electrolytes.

range diffusion models [57].

$$\Gamma(Q) = D_i Q^2 \quad (11)$$

3. Results and discussion

3.1. Specific capacitance and ESR

The cyclic voltammograms (CVs) in Fig. 1a) reveal distinct capacitive behaviors for the three materials, with rGOag-KOH exhibiting the highest specific capacitance (68 F/g), followed by ACNagKOH (32 F/g) and ACMagKOH (25 F/g). The near-rectangular shape of the CVs, particularly for rGOag-KOH, indicates dominant electric double-layer (EDL) behavior with minimal faradaic contributions, consistent with its low ESR, which facilitates efficient ion diffusion and charge storage. In contrast, the slightly rounded corners observed in the CV of ACMag-KOH suggest a higher ESR, leading to increased energy losses and reduced current response, thereby lowering its capacitance. The intermediate performance of ACNagKOH, with a moderately rectangular CV, reflects a balance between ESR and capacitive behavior, with its lower ESR ($15.1 \Omega \text{ cm}^2$) contributing to a more ideal voltammetric profile compared to ACMagKOH. These trends are illustrated in Fig. 1b), where ACNag-ChClEG demonstrates the highest specific capacitance (34 F/g), followed by ACMag-ChClEG (17 F/g) and rGOag-ChClEG (8 F/g). The quasi-rectangular CVs, particularly for ACNag-ChClEG, indicate dominant EDL behavior with minimal faradaic contributions, consistent with its relatively low ESR. Conversely, the pronounced rounding in the CV of rGOag-ChClEG suggests a higher ESR, leading to significant energy losses and reduced capacitance. These results align with the principles discussed in the literature, where low ESR correlates with higher capacitance and more ideal voltammetric profiles, while higher ESR distorts the CV shape and diminishes capacitive performance [58]. This comparative analysis underscores the critical role of ESR and electrolyte composition in optimizing the electrochemical performance of supercapacitors, as they directly influence both capacitance and voltammetric behavior across different systems.

Turning to the analysis of the discharge region in the voltammograms of the ChClEG-soaked SC, even if a faradaic peak is not observed, the rounding of the curve is more evident, which indicates that the ESR values are higher. The GCD curves of ACMaglom, ACNag and rGOag EDLCs in aqueous KOH and eutectic ChClEG electrolytes, obtained with a current density of 10 mA/g chosen to operate in a range according to the maximum current reached as detected in the voltammograms, are depicted in Fig. 2a) and b). Typical isosceles or quasi-isosceles triangular

curves are observed [59].

Table 2 presents the calculated specific capacitance, equivalent series resistance (ESR), and energy density for the symmetric supercapacitor devices. The analysis of these interconnected parameters reveals a comprehensive picture of the electrochemical performance. The specific capacitance of ACMagKOH is 22 % lower than that of ACNagKOH and 63 % lower than rGOagKOH. This trend is directly mirrored in the energy density, where ACMagKOH (3.5 Wh/kg) is 20 % and 63 % lower than ACNagKOH (4.4 Wh/kg) and rGOagKOH (9.4 Wh/kg), respectively, consistent with the relationship $E = \frac{1}{2} CV^2$.

The equivalent series resistance (ESR) provides crucial insights into the efficiency of charge transfer. The ranking ACNagKOH < rGOagKOH < ACMagKOH for ESR confirms that ACNag exhibits the most efficient ion transport, a key factor contributing to its balanced performance in both capacitance and energy density. The high ESR of ACMagKOH (79 % and 70 % higher than ACNagKOH and rGOagKOH, respectively) signifies significant resistive losses, which detrimentally impact its power delivery and energy storage capabilities.

In the ChClEG electrolyte, the performance trends shift, highlighting the critical role of electrolyte compatibility. ACNagChClEG achieves the highest specific capacitance (34 F/g) and consequently the highest energy density (4.7 Wh/kg) in this system. Remarkably, its energy density in ChClEG is comparable to its performance in KOH (4.4 Wh/kg), underscoring its exceptional compatibility with the viscous eutectic electrolyte. This is facilitated by its low ESR ($15.6 \Omega \text{ cm}^2$), which is an order of magnitude lower than that of rGOagChClEG ($624.8 \Omega \text{ cm}^2$). The

Table 2

Specific capacitance of supercapacitors composed of laminated electrodes of commercial activated carbon ACN with and reduced graphene oxide rGO with potassium hydroxide and eutectic electrolytes ChClEG. Data were collected using a scan rate of 1 mV/s and a current density of 10 mA/g.

Material electrode	Electrolyte	Specific Capacitance (F/g)	ESRs ($\Omega \text{ cm}^2$)	Energy Density (Wh/kg)
rGOag	KOH 1M	68 ± 3.4	21.7 ± 0.9	9.4 ± 0.5
ACMag	KOH 1M	25 ± 1.3	72.1 ± 0.4	3.5 ± 0.2
ACNag	KOH 1M	32 ± 1.6	15.1 ± 0.2	4.4 ± 0.2
rGOag	ChClEG (1:2)	8 ± 0.4	624.8 ± 71.5	1.1 ± 0.1
ACMag	ChClEG (1:2)	17 ± 0.9	87.0 ± 0.4	2.4 ± 0.1
ACNag	ChClEG (1:2)	34 ± 1.7	15.6 ± 7.6	4.7 ± 0.2

catastrophically high ESR of rGOagChClEG directly explains its poor energy density (1.1 Wh/kg), as a significant portion of the stored energy is dissipated as heat. ACMagChClEG shows intermediate performance, with an energy density of 2.4 Wh/kg, constrained by its moderate capacitance and elevated ESR compared to ACNag.

These findings underscore a fundamental structure-property-performance relationship: hierarchical slit-shaped pores (ACNag) facilitate low ESR and high capacitance, translating to robust energy density across different electrolytes. In contrast, ink-bottle pores (ACMag) and agglomerated structures with limited mesoporosity (rGOag) lead to higher ESR and severe performance degradation, particularly in viscous electrolytes, which is unequivocally reflected in their low energy density.

3.2. Brunauer-Emmett-Teller nitrogen adsorption/desorption technique

In order to understand the somewhat controversial results of the electrochemical results, BET analysis and nitrogen adsorption isotherms (NAI) were performed on the activated carbon and reduced graphene oxide powders to determine the surface area and porosity of the samples [60]. Table 3 presents a comparison of BET surface area, pore volume and pore size and their relationship with the molecule sizes and ionic ratio of ChClEG and $K^+ - HO^-$ electrolytes, respectively.

The N_2 adsorption-desorption isotherm in Fig. 3a) for coconut shell activated carbon (ACMp) corresponds to a Type I (IUPAC) isotherm with H4 hysteresis, indicating a material dominated by microporosity and limited mesoporosity in narrow or slit-like structures [61], as confirmed by the SEM image in Fig. 3b). The rapid adsorption at low relative pressures ($P/P_0 < 0.1$), with an adsorbed volume of $\sim 40 \text{ cm}^3/\text{g}$ STP, confirms high microporosity ($0.196 \text{ cm}^3/\text{g}$, t-plot). The irreversible hysteresis in the $0.4 < P/P_0 < 0.8$ range suggests disordered mesopores or complex geometries ("ink-bottle pores"), which may hinder ionic diffusion in viscous electrolytes. The BET surface area was $410.72 \text{ m}^2/\text{g}$ supported by a bimodal pore distribution ($\sim 18 \text{ \AA}$ and $\sim 750 \text{ \AA}$).

From Fig. 3c) it is seen that activated carbon ACNp (Nuclear Ltd.) has an adsorption-desorption isotherm of N_2 type IV with hysteresis of H4 [62], which can be confirmed by the SEM image in Fig. 3d). Its BET surface area is $592.65 \pm 8.02 \text{ m}^2/\text{g}$ calculated in the linear range ($P/P_0 = 0.05\text{--}0.30$), together with a total pore volume of $0.550 \text{ cm}^3/\text{g}$. The microporosity ($0.158 \text{ cm}^3/\text{g}$, $305.33 \text{ m}^2/\text{g}$) ensures a high density of active sites, while the mesopore distribution (peak at $\sim 3.8 \text{ nm}$, BJH) optimizes ion diffusion, balancing capacitance and rate capability. This hierarchical micro/mesopore combination, along with an average pore diameter of $37.15 \text{ \AA}$, suggests robust performance in high-power applications, where mechanical stability and rapid charge/discharge kinetics are critical.

The reduced graphene oxide (rGO) exhibits a Type IV N_2

Table 3

Comparison of BET pore sizes and Structural Attributes of the powdered samples.

Parameter	ACMp	ACNp	rGO
BET Surface Area (m^2/g)	$411 \pm 7 \text{ m}^2/\text{g}$	$593 \pm 8 \text{ m}^2/\text{g}$	$20 \pm 1 \text{ m}^2/\text{g}$
Pore Volume (cm^3/g)	0.196 (micro) + 0.188 (meso)	0.550 (total: 0.158 micro + 0.415 meso)	0.010 (meso)
Pore Size ($\text{\AA}$)	~ 18 (micro)	~ 38 (meso)	20–50 (meso)
Isotherm Type	Type I	Type IV	Type IV
Hysteresis Type	H4 ("inkbottle" pores)	H4 (slit-shaped pores)	H3 (interparticle pores)
Pore Geometry	Narrow mesopores + "inkbottle" micropores	Hierarchical slit-shaped pores	Slit-shaped mesopores (stacked sheets)
Electrolyte Compatibility	Optimal for 1 M KOH (OH^- : $\sim 3.6 \text{ \AA}$)	Suitable for both 1 M KOH and ChClEG	Better for ChClEG (larger ions: 5–10 $\text{\AA}$)

adsorption-desorption isotherm with H3 hysteresis (IUPAC) (Fig. 3e), indicative of mesoporous materials (2–50 nm) with a lamellar structure and interparticle porosity [63] (Fig. 3f), ideal for electrolyte diffusion in supercapacitors. Its BET surface area of $20.13 \text{ m}^2/\text{g}$, yet modest compared to standard graphene, suggests sheet agglomeration or residual functional groups post-reduction. The pore size distribution (BJH) reveals dominant mesoporous volume ($0.008\text{--}0.010 \text{ cm}^3/\text{g}$) in the 20–50 $\text{\AA}$ range.

3.3. Distinguishing the volatile elements remaining from the activation process on powdered and agglomerated samples by TG-FTIR-MS

To gather more information on the activation process residues of the powdered samples and the electrode forming process, we conducted thermal analysis coupled with infrared spectroscopy and mass spectrometry under nitrogen atmosphere. The mass spectrometry data for the ACMp, ACNp and rGO exhibit a consistent decline in ion currents for fragments m/z 15–44 with increasing temperature, indicating progressive desorption and thermal decomposition of surface-bound species, which aligns with the TG-derived minimal mass loss and the FTIR-observed dominance of low-temperature processes. The QMID signals for each m/z number can be corroborated in the supplementary information. We estimated that the weight loss in ACMp and ACNp corresponds to volatile components that can evaporate at low temperatures ($<100^\circ\text{C}$) (see Fig. S3 in the complementary data). These volatile compounds can be water molecules, and functional groups like lignin (carbonyl, carboxylic and hydroxyl groups), present on the porous surface of the samples [64,65].

Based on the dTGA curve, thermal stability order of the samples was as follow: ACNp > ACMp > rGO. ACNp shows the highest thermal stability with the lowest mass loss (2.9 %). ACMp follows with slightly higher mass loss (3.8 %). rGO exhibits the highest mass loss (20.8 %) due to its functional groups and adsorbed moisture. Residual mass: All samples retain a high percentage of their mass ($>79\%$) after heating to 600°C , which is expected for carbon-based materials in an inert atmosphere [64,65]. The low mass loss of ACNp and ACMp suggests they are highly stable and suitable for high-temperature applications [64]. The higher mass loss of rGO indicates it may require additional processing (e.g., further reduction or functionalization) to improve its thermal stability.

The FTIR (Fig. 4a) results for ACMp reveal a complex evolution of gaseous species over key temperatures, correlating with the mass loss events observed in the TG-DTG analysis. At 37°C , a mass loss of $\sim 96.4\%$ is attributed to the release of adsorbed water and volatile organic compounds (VOC), as evidenced by broad FTIR peaks in the $3000\text{--}3600 \text{ cm}^{-1}$ (O-H stretching) and $1600\text{--}1700 \text{ cm}^{-1}$ (H-O-H bending) regions, alongside minor C-H stretching ($2800\text{--}3000 \text{ cm}^{-1}$) from organic fragments. This reflects the hygroscopic nature of the material and the low-temperature volatilization of labile components. As the temperature increases to 102°C , 355°C and 555°C , the spectra show progressive decomposition of oxygenated functional groups (e.g. C=O at $\sim 1700 \text{ cm}^{-1}$, C-O-C at $\sim 1200 \text{ cm}^{-1}$) and aromatic C=C bonds ($\sim 1600 \text{ cm}^{-1}$), releasing CO_2 (sharp peaks $\sim 2350 \text{ cm}^{-1}$) and CO ($\sim 2100 \text{ cm}^{-1}$) [64,65]. The 600°C spectrum shows degradation of the remaining carbonaceous structure, $<4\%$ combined, with weak peaks from polycyclic aromatic hydrocarbons.

The FTIR results (Fig. 4b) for ACNp show that at 37°C , the $>90\%$ of the total mass loss is also attributed to the release of adsorbed water and VOC, as evidenced by broad O-H stretches ($3000\text{--}3600 \text{ cm}^{-1}$) and C-H vibrations ($2800\text{--}3000 \text{ cm}^{-1}$). As the temperature increases to 119°C , 355°C and 555°C , the spectra show progressive decomposition of oxygenated functional groups, with prominent peaks for CO_2 ($\sim 2350 \text{ cm}^{-1}$) and CO ($\sim 2100 \text{ cm}^{-1}$), alongside aromatic C=C ($\sim 1600 \text{ cm}^{-1}$) and C=O ($\sim 1700 \text{ cm}^{-1}$) bonds, indicating oxidative cleavage of carbonaceous structures. The 600°C spectrum confirms residual carbon matrix decomposition, with weak polycyclic aromatic signals. In

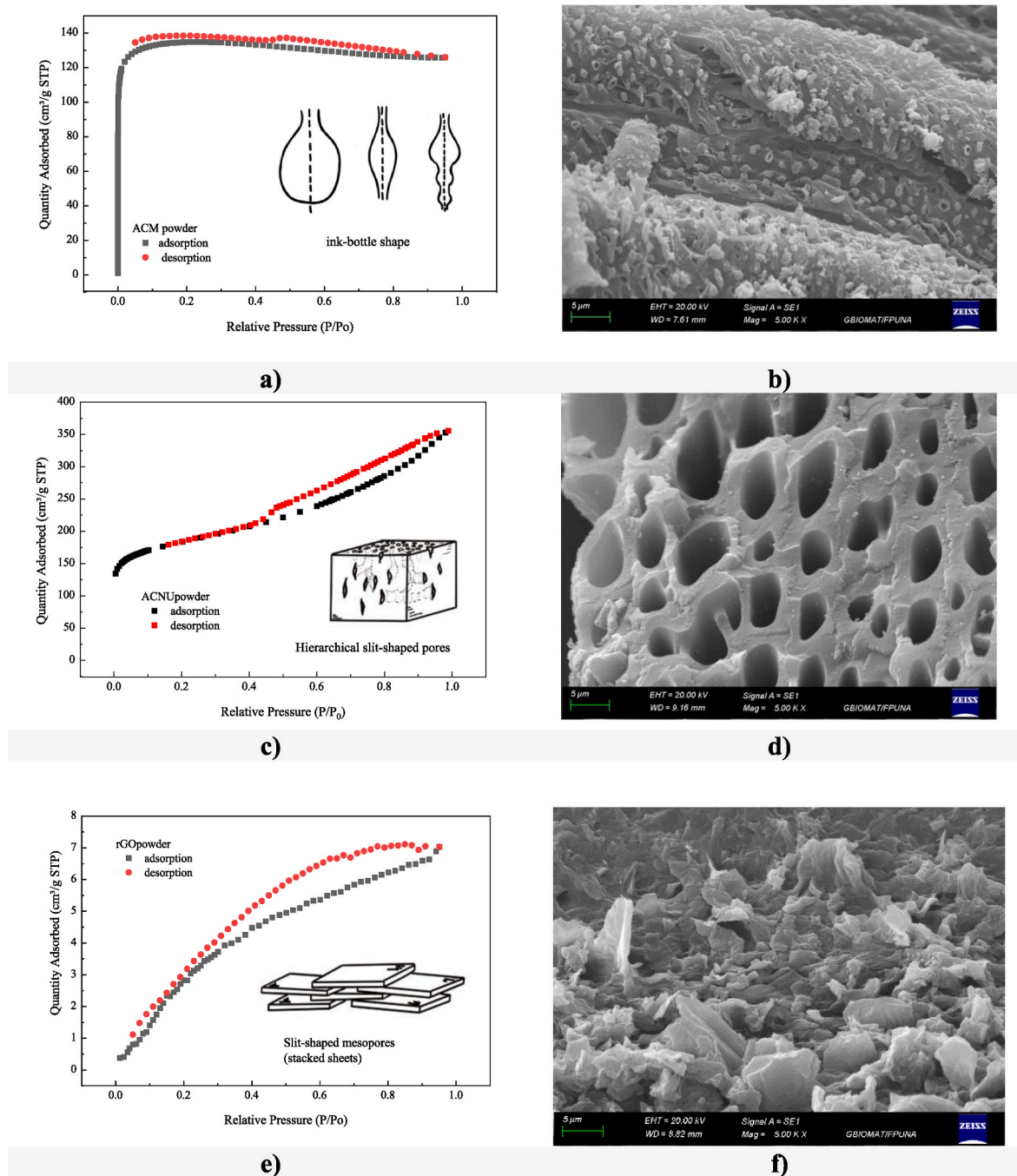


Fig. 3. The apparent decrease in the desorption branch at very high P/P_0 is an instrumental artifact related to the free space measurement step and does not reflect a material property.

particular, the 555 °C and 600 °C spectra show enhanced CO₂/CO peaks (e.g. 1418 cm⁻¹, 1507 cm⁻¹) and aromatic C=C degradation.

The FTIR results for rGO (Fig. 4c) reveal a thermally stable material with gas evolution occurring primarily at higher temperatures, consistent with its reduced graphene oxide structure. At 260 °C, minor mass loss (~5–10 % of the total) is attributed to the release of residual oxygen functionalities (e.g. C=O at ~1700 cm⁻¹, C-O at ~1200 cm⁻¹) and adsorbed water (broad O-H stretch at 3000–3600 cm⁻¹). The dominant mass loss occurs at 555 °C (accounting for most of the total mass loss), where intense peaks for CO₂ (~2350 cm⁻¹) and CO (~2100 cm⁻¹) dominate, indicating thermal decomposition of more stable oxygen groups (e.g. carboxyl, epoxy) and graphitic domain fragmentation. FTIR spectra at intermediate temperatures (e.g. 355 °C, 458 °C) show

progressive weakening of oxygen-related peaks (e.g. 1418 cm⁻¹, 1507 cm⁻¹), while the 600 °C spectrum confirms almost complete degradation of labile moieties, leaving only traces of polyaromatic hydrocarbons (weak C=C stretches ~1600 cm⁻¹). The 555 °C event coincides with the DTG peak and represents the primary mass loss phase (~70–80 % of the total), while the 260 °C transition contributes marginally (<15 %), reflecting the resistance of rGO to low-temperature degradation. The high-temperature dominance of CO₂/CO evolution highlights the structural stability of the material, with a residual mass loss (<5 %) at 600 °C associated with the rearrangement of the carbon matrix.

Table 4 synthesizes the thermal degradation mechanisms of coconut shell-derived activated carbons (ACMp, ACNp) and reduced graphene oxide (rGO), correlating mass spectrometry (MS), thermogravimetry

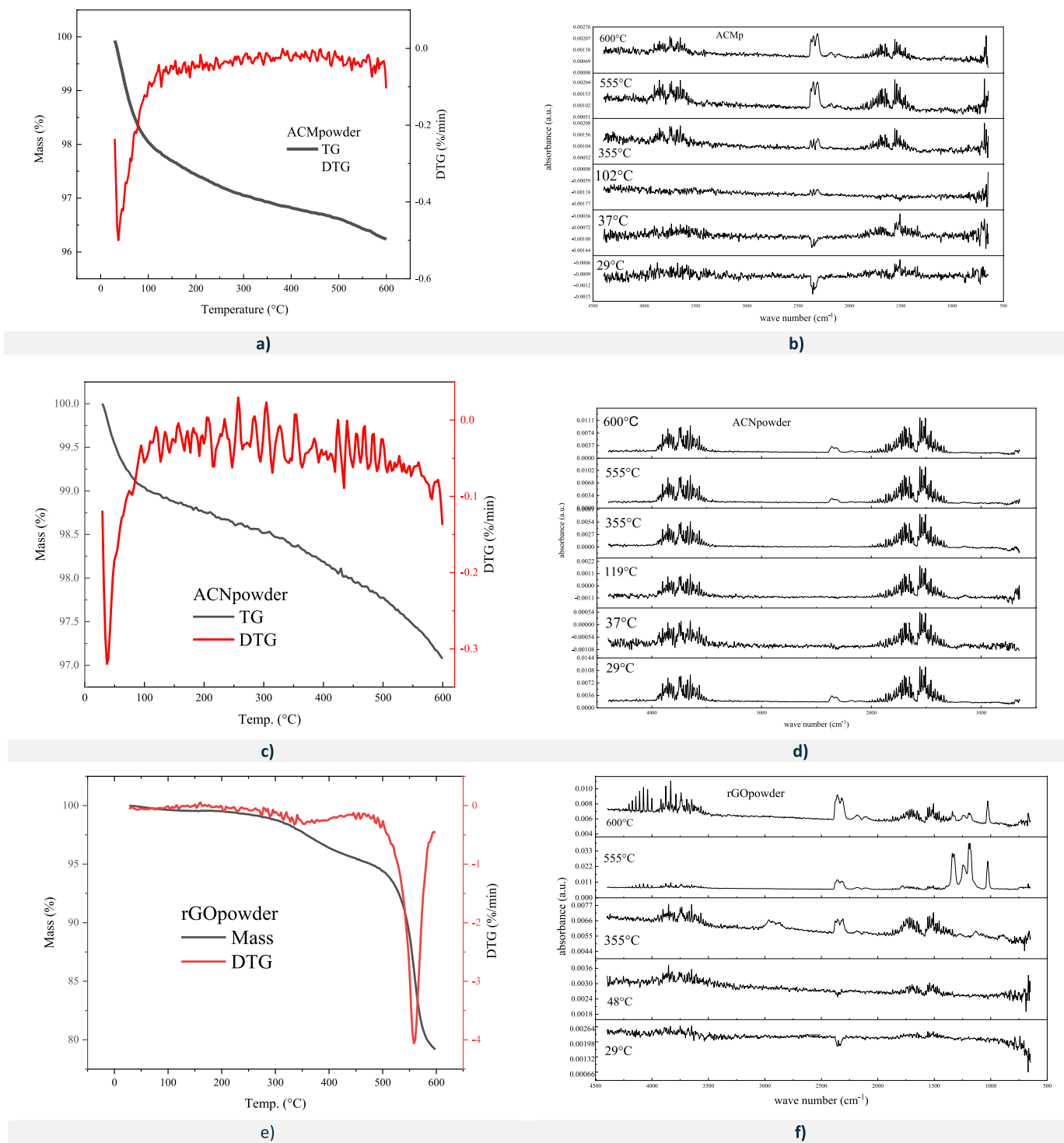


Fig. 4. TG thermogram and FTIR spectra of ACMp, ACNp, and rGOp.

(TG), and FTIR data. ACMp and ACNp exhibit dominant low-temperature mass loss (37 °C, >95 %) from physisorbed H₂O and volatile organics (C-H stretches), reflecting their hygroscopic nature and microporous structure. Minimal high-temperature CO₂/CO evolution (<5 % combined at 355–555 °C) confirms limited oxidative degradation of oxygen functionalities (C=O, C-O). In contrast, rGOp demonstrates thermal resilience below 260 °C, with 70 % mass loss at 555 °C from CO₂ release (*m/z* 44), indicative of oxidative cleavage of carboxyl/epoxy groups (FTIR: 1700 cm⁻¹). Residual mass trends (ACMp: 96.24 %, rGOp:

79.17 %) align with structural integrity differences: ACM/ACN retain carbon matrix stability, while rGO's graphitic backbone undergoes partial fragmentation. The absence of aromatic C=C degradation (1600 cm⁻¹) in ACM/ACN underscores their chemical inertness, whereas rGO's residual polyaromatic signatures (600 °C) highlight incomplete graphitic reorganization. This integrated analysis underscores the role of surface chemistry and porosity in dictating thermal stability across carbonaceous materials.

Table 4

Correlation of thermal degradation profiles, evolved gaseous species, and functional group decomposition for ACMP, ACNp, and rGO.

Compound	<i>m/z</i>	Bands(cm^{-1})	ACMp (T (°C), Mass (%))	ACNp (T (°C), Mass (%))	rGO (T (°C), Mass (%))
H ₂ O	18	3000–3600 (O-H stretch) 1600–1700 (H-O-H bend)	37 °C (96.4 %) 119 °C (3 %) 355 °C (0.6 %)	37 °C (95.3 %) 102 °C (4 %) 260 °C (0.7 %)	48 °C(5 %) 260 °C (2 %) 555 °C (1 %)
CO ₂	44	2350 (asym. stretch) 670 (bend)	355 °C (4 %) 555 °C (3 %) 600 °C (1 %)	102 °C (2 %) 355 °C (3 %) 600 °C (1 %)	260 °C (3 %) 458 °C (5 %) 555 °C (70 %)
CO	28	2100–2200 (stretch)	355 °C (2 %) 555 °C (1 %) 600 °C (0.5 %)	355 °C (1 %) 555 °C (0.5 %) 600 °C (0.2 %)	458 °C (1 %) 555 °C (15 %) 600 °C (5 %)
CH ₄	16	1300(C-H bend) 3000(C-H stretch)	119 °C (0.1 %) 355 °C (0.2 %)	37 °C (0.1 %) 102 °C (0.1 %)	–
Volatile Organics	15–30 (fragments)	2800–3000 (C-H stretch) 1700(C=O)	37 °C (1.5 %) 119 °C (0.5 %)	37 °C(1 %) 102 °C (0.3 %)	–
Oxygen Groups (C=O, C- O)	–	1700 (C=O) 1200 (C-O)	355 °C (2 %) 555 °C (1 %)	102 °C (1 %) 355 °C (2 %)	260 °C (1 %) 458 °C (2 %) 555 °C (10 %)
Aromatic C=C	–	1600 (C=C stretch)	555 °C (0.5 %) 600 °C (0.3 %)	600 °C (0.2 %)	–

3.4. Connecting structural and chemical information obtained for the powder samples

The comparative evaluation of ACNag, ACMag, and rGOag electrodes highlights critical structure-performance relationships governed by BET-derived porosity, PTFE binder interactions, and electrolyte ion dynamics. ACNag's hierarchical slit-shaped pores and high pore volume enable optimal capacitance and low ESR, facilitated by unrestricted ion penetration (K^+/OH^- : ~ 0.13 nm; ChCl-EG: ~ 0.3 – 0.4 nm) and minimal PTFE-induced pore occlusion. PTFE's molecular structure, characterized by a helical conformation with C–F bond lengths of ~ 0.13 nm and a van der Waals radius of ~ 0.27 nm for fluorine atoms, creates localized hydrophobic domains that influence pore accessibility, particularly in mesoporous systems [66,67]. ACMag's inkbottle mesopores and PTFE-aggravated resistive losses result in ion-trapping and restricted diffusion, limiting capacitance (25 F/g in KOH, 17 F/g in ChCl-EG). The ionic radii of K^+ (0.133 nm) and OH^- (0.137 nm) in KOH allow efficient diffusion through micropores, while the larger hydrated ions in ChClEG (e.g., choline cation: ~ 0.43 nm, chloride: ~ 0.33 nm, and ethylene glycol complexes) face kinetic limitations in non-hierarchical pores, as shown in studies linking ion confinement to capacitive performance [68,69]. rGOag's sparse mesoporosity (0.010 cm^3/g) and PTFE-blocked pathways lead to pseudocapacitance-driven performance in KOH (68 F/g) but catastrophic failure in ChCl-EG (8 F/g, ESR: 624.8 $\Omega \text{ cm}^2$), underscoring the critical role of ion-pore size matching and binder

distribution. Recent studies emphasize that PTFE's nanoscale fibrillar networks exacerbate pore occlusion for larger ions, while its chemical inertness stabilizes interfaces in aqueous systems [66]. These findings align with advanced models correlating electrolyte ion dynamics (e.g., solvation shell effects, viscosity) with hierarchical pore design to mitigate size-exclusion losses in complex electrolytes like ChClEG [68,69]. These results demonstrate that optimizing the electrode preparation—through higher-temperature treatments to remove impurities, reduced PTFE content, and tailored pore hierarchy—can significantly enhance electrochemical performance by improving ion accessibility and minimizing resistive losses.

3.5. Elucidating the charge storage mechanism: EDLC and pseudocapacitance

Our results demonstrate that the performance of the studied supercapacitors is governed by a hybrid charge storage mechanism, where Electric Double-Layer Capacitance (EDLC) and Pseudocapacitance contribute synergistically, with their predominance dictated by pore architecture, electrode surface chemistry, and electrolyte compatibility.

The electrochemical performance, pore architecture, and surface chemistry data collectively indicate that the charge storage in the studied supercapacitors is governed by a hybrid mechanism, where electric double-layer capacitance (EDLC) and pseudocapacitance contribute synergistically. The predominance of each mechanism is dictated by the specific combination of electrode material and electrolyte.

3.5.1. Evidence for EDLC storage

The quasi-rectangular shape of the cyclic voltammograms (Fig. 1), particularly pronounced for rGOag-KOH and ACNag-ChClEG, is a hallmark of EDLC behavior, where charge storage is physical and non-faradaic [70]. This mechanism is dominant in materials with high accessible surface area and porosity. BET data (Table 3) corroborate this: ACNp, with its high surface area (593 m^2/g) and hierarchical porosity, shows excellent capacitive performance in both electrolytes, facilitating efficient electric double-layer formation. The direct relationship between micropore volume (crucial for EDLC) and capacitance in KOH (e.g., ACNagKOH: 32 F/g) supports this contribution [71].

3.5.2. Evidence for pseudocapacitive contribution

Deviations from ideal rectangularity in the CVs, such as the slightly rounded corners in ACMag-KOH, suggest the presence of faradaic processes. The TG-FTIR-MS analysis (Table 4) is key here, as it identifies the presence and decomposition of oxygenated functional groups (C=O, C-O) on the carbon surface. These groups, residual from the precursors and activation processes, can participate in fast, reversible redox reactions, generating a pseudocapacitive contribution [70,72]. The exceptional capacitance of rGOag-KOH (68 F/g), despite its low surface area (20 m^2/g), can only be explained by a significant pseudocapacitive contribution, likely from the residual functional groups in the reduced graphene oxide.

3.5.3. Hybrid mechanism and the role of porosity

We propose that the total capacitance (C_{total}) is the sum of the electric double-layer capacitance (C_{EDLC}) and the faradaic pseudocapacitance (C_{pseudo}). The pore structure is a determining factor in this synergy. The micropores (< 2 nm) in ACMP and ACNp are the primary sites for EDLC and can accommodate surface pseudocapacitive reactions. The mesopores (2–50 nm), particularly abundant in ACNp, act as “ionic highways”, ensuring rapid electrolyte transport to the active sites, which is crucial for sustaining pseudocapacitance at high scan rates and in viscous electrolytes like ChClEG [71]. The “ink-bottle” geometry in ACMP, identified by BET, restricts this transport, limiting access to storage sites and resulting in lower capacitance and higher ESR.

3.5.4. Linking storage mechanism to electrochemical performance

This hybrid model explains the performance trends across different electrolytes. In aqueous KOH, the compatibility between small ion size and pore structure allows both EDLC and pseudocapacitance to contribute effectively, leading to higher overall capacitance. In the viscous ChClEG electrolyte with larger ions, the performance becomes heavily dependent on the electrode's ability to facilitate ion access to pseudocapacitive sites, which is optimal in hierarchical slit-shaped pores (ACN) and severely limited in restricted geometries (ACM) or agglomerated structures (rGO).

In summary, the integration of our electrochemical, structural, and thermal characterizations confirms a storage model where EDLC and pseudocapacitance coexist. The relative contribution of each mechanism is finely tuned by the pore hierarchy, surface chemistry, and electrolyte-electrode compatibility.

3.6. Neutron spectroscopy: QENS

Fig. 5 presents a comparative analysis of QENS spectra for ACMagDry (Fig. 5a) and ACMagKOH (Fig. 5b) at two representative momentum transfers: $Q = 0.55 \text{ \AA}^{-1}$ (low- Q) and $Q = 1.55 \text{ \AA}^{-1}$ (high- Q). Both spectra are well-described by a delta function (elastic scattering) and a single Lorentzian (quasi-elastic broadening), with residuals symmetrically distributed around zero, validating the fitting model. Notably, the quasi-elastic component in ACMagKOH exhibits a broader Lorentzian profile compared to ACMagDry, particularly at high- Q , consistent with its higher extracted translational diffusion coefficient (D_t). This broadening aligns with the Q^2 -dependence of the HWHM (Γ), reflecting enhanced diffusive motion in the presence of KOH electrolyte. The intensity of the elastic peak (delta function) is marginally reduced in ACMagKOH, suggesting increased dynamics due to hydration effects from the electrolyte, whereas ACMagDry retains stronger elastic contributions, indicative of restricted motion in the absence of solvent. The higher total counts in ACMagKOH spectra (e.g., 275 vs. 250 at $0.55 \text{ \AA}^{-1}$) may arise from improved proton mobility or electrolyte-mediated pore

accessibility, corroborating its superior electrochemical performance (25 F/g vs. lower capacitance in dry conditions). These observations underscore the critical role of electrolyte in modulating confined water dynamics within the mesoporous carbon matrix, as further supported by BET and TGA-FTIR-MS data highlighting pore geometry and hydration stability.

The quasi-elastic neutron scattering (QENS) analysis of ACMagKOH and ACMagDry electrodes reveals distinct dynamical behaviors linked to their structural and compositional differences. For ACMagKOH (with KOH electrolyte), the linear dependence of HWHM (Γ) on Q^2 (Fig. 6a) confirms Fickian diffusion, yielding a translational diffusion coefficient ($D_t = 1.24 \pm 0.09 \times 10^{-9} \text{ m}^2/\text{s}$), calculated from the slope ($\Gamma = \hbar D_t Q^2$). In contrast, ACMagDry (without electrolyte) exhibits a marginally lower ($D_t = 1.14 \pm 0.09 \times 10^{-9} \text{ m}^2/\text{s}$), reflecting an 8.8 % reduction in diffusivity. Both values are significantly lower than bulk water ($D_t = 2.49 \times 10^{-9} \text{ m}^2/\text{s}$) reported by Berg et al. (2017) [73], highlighting confinement effects within the porous carbon matrix. The BET analysis supports this, showing a mesoporous structure (pore size $\sim 18 \text{ \AA}$, surface area $411 \text{ m}^2/\text{g}$) with “ink-bottle” pore geometry, which restricts molecular motion. The higher D_t for ACMagKOH likely stems from enhanced hydration due to KOH, improving pore accessibility, whereas ACMagDry relies on residual moisture, as evidenced by TGA-FTIR-MS detecting H_2O desorption up to 355°C . The EISF trends (Fig. 6b) further suggest localized dynamics, with ACMagDry showing a steeper decline in EISF with Q , indicative of increased confinement or restricted motion in the absence of electrolyte. Electrochemically, ACMagKOH achieves a specific capacitance of 25 F/g with moderate ESR ($72 \text{ }\Omega\text{cm}^2$), likely limited by PTFE fibrils obstructing micropores. The combined QENS and structural data advocate a diffusion model incorporating both translational motion (Q^2 -dependent Γ) and localized dynamics (EISF trends), consistent with hindered diffusion in mesoporous media. These findings underscore the critical role of electrolyte presence and pore architecture in modulating ion transport, with implications for optimizing carbon-based supercapacitors. In Supplementary information are presented the QENS spectra for ACMagChClEG (a), rGOagChClEG (b), and ACNagChClEG (c), highlighting distinct elastic

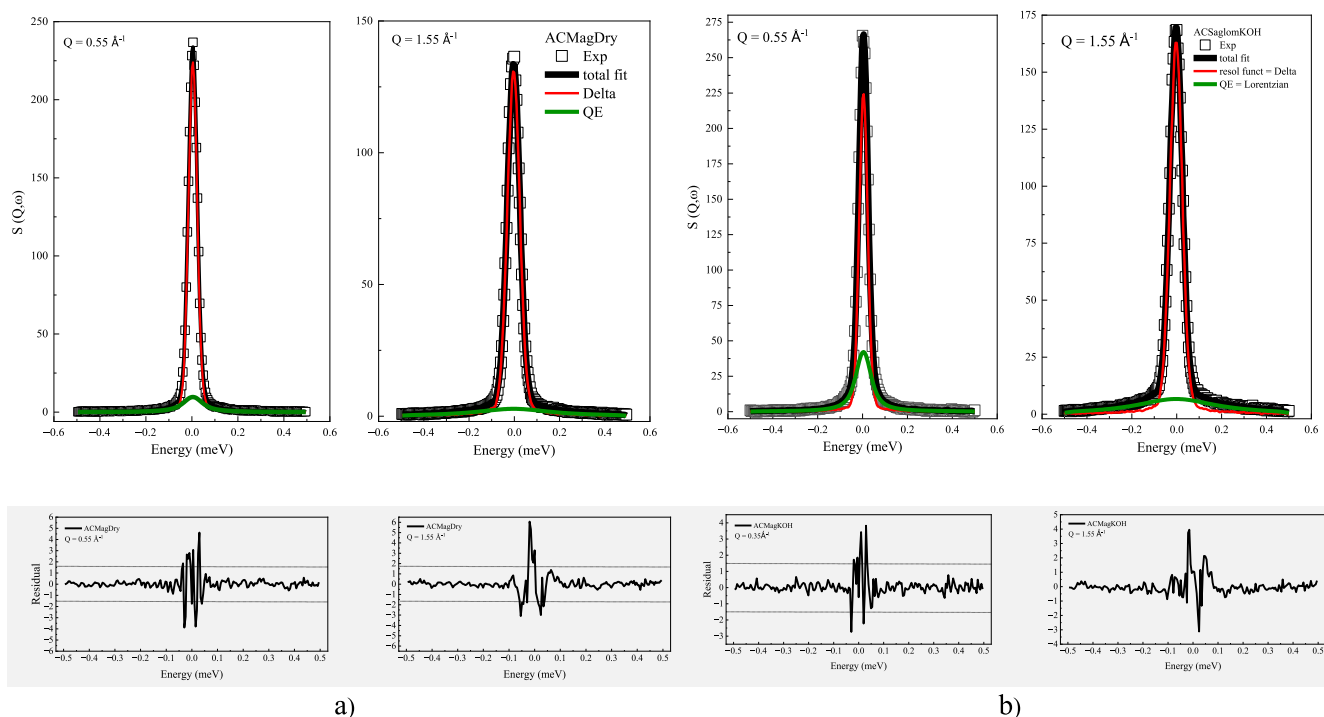


Fig. 5. Comparison of the QE signal for the a) ACMagDry and b) ACMagKOH between the first and the last Q values $Q_2 = 0.55 \text{ \AA}^{-1}$ – $Q_7 = 1.55 \text{ \AA}^{-1}$. It is noted that the fitting is good by the symmetrical random residual distribution around the zero level.

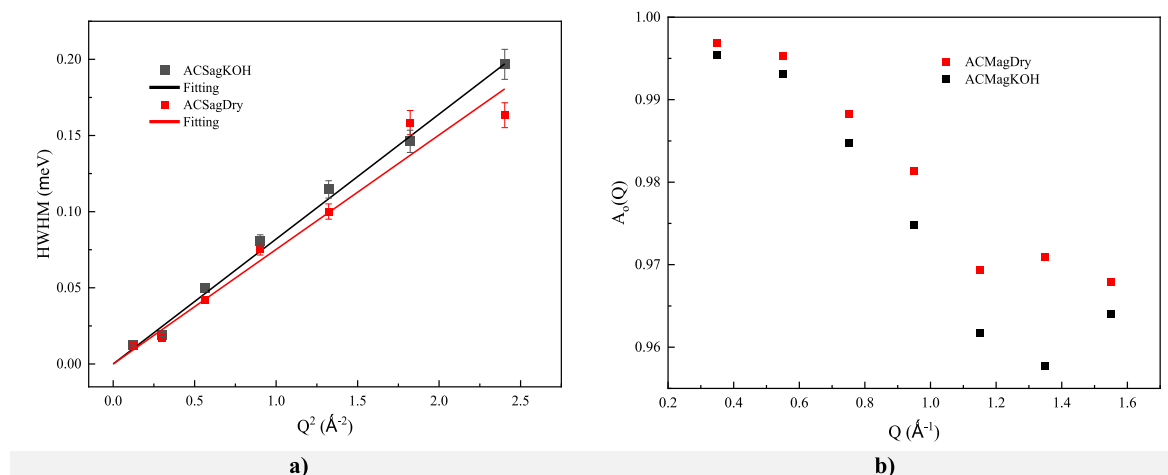


Fig. 6. a) comparison of the QE dependence on Q values b) comparison EISF extracted from de QENS data for Dry electrode and the electrode with KOH electrolyte. The data were fitted using the equations described in the text.

(delta function) and quasi-elastic (Lorentzian) contributions across varying Q -ranges.

For ACNagChCIEG (see SI), the elastic peak dominates at both ($Q = 0.75 \text{ \AA}^{-1}$) and ($1.55 \text{ \AA}^{-1}$), with a minimal quasi-elastic component, suggesting highly restricted dynamics consistent with its unresolved HWHM (below instrumental resolution). In contrast, ACNagChCIEG (see SI) exhibits a reduced elastic intensity at lower ($Q = 0.35 \text{ \AA}^{-1}$) and a marginally broader quasi-elastic profile at high Q , indicative of slightly enhanced mobility, though still unresolved due to the sub-resolution HWHM. The rGOagChCIEG spectra (see SI) display the weakest quasi-elastic signal, with elastic contributions persisting even at ($Q = 1.55 \text{ \AA}^{-1}$), reflecting extreme spatial confinement or near-static behavior. Symmetric residuals around zero in all fits validate the model (delta + Lorentzian), though the unresolved broadening underscores dynamics slower than the spectrometer's temporal resolution (~ 12 ps). These observations align with the earlier HWHM analysis, reinforcing that ACNagChCIEG and ACNagChCIEG experience differing degrees of confinement (ink-bottle vs. slit-shaped pores), while rGOagChCIEG's stacked-sheet morphology imposes severe restrictions, effectively suppressing detectable quasi-elastic scattering. The data collectively emphasize the role of pore geometry in modulating localized motions, even when translational diffusion remains unresolved. The QENS data for ACNagChCIEG, ACNagChCIEG, and rGOagChCIEG (Fig. S7d) reveal unresolved quasi-elastic broadening, as their HWHM values fall below the FOCUS spectrometer's resolution (0.054 meV), indicating dynamics slower than ~ 12 ps or spatially restricted motion. This precludes direct estimation of translational diffusion coefficients (D_t), as the unresolved Γ implies D_t values $< 1 \times 10^{-10} \text{ m}^2/\text{s}$ —over an order of magnitude lower than ACNagKOH ($D_t = 1.24 \times 10^{-9} \text{ m}^2/\text{s}$) and ACNagDry ($1.14 \times 10^{-9} \text{ m}^2/\text{s}$). Despite this, ACNagChCIEG exhibits a 100 % higher specific capacitance (34 F/g vs. 17 F/g for ACNagChCIEG) and 82 % lower ESR (15.6 vs. 87 Ωcm^2), attributed to its hierarchical slit-shaped pores (592 m^2/g surface area, $\sim 38 \text{ \AA}$ pores) enabling better ion accessibility compared to ACNag's ink-bottle geometry ($\sim 18 \text{ \AA}$ pores). Conversely, rGOagChCIEG's poor performance (8 F/g, 625 Ωcm^2) aligns with its minimal surface area (20 m^2/g) and inadequate pore structure for ChCIEG ions (5–10 $\text{\AA}$). TGA-FTIR-MS data further correlate these trends: ACNag retains 4 % adsorbed H_2O at 102 $^\circ\text{C}$ (vs. 3 % for ACNag at 119 $^\circ\text{C}$), suggesting stabilized hydration layers that mitigate pore blockage. These results emphasize that while hierarchical porosity enhances charge storage via surface accessibility, unresolved QENS signals highlight diffusion limitations in viscous ChCIEG electrolytes, underscoring a decoupling between capacitive

performance and ion mobility in highly confined systems.

The QENS spectra for ACNagDry, ACNagKOH, rGOagDry, and rGOagKOH (Supplementary information) lack resolvable quasi-elastic (QE) signals, necessitating fits using only a delta function (elastic scattering), which precludes extraction of HWHM or EISF parameters. This contrasts sharply with ACNagKOH and ACNagDry, where measurable QE broadening enabled quantification of translational diffusion coefficients ($D_t \sim 10^{-9} \text{ m}^2/\text{s}$). The absence of QE components implies dynamics slower than the FOCUS spectrometer's temporal resolution (≥ 12 ps) or motions confined to spatial scales undetectable within the instrumental Q -range. Notably, rGOagKOH exhibits the highest specific capacitance (68 F/g) and low ESR (21.7 Ωcm^2) despite its negligible QE signal, a paradox attributed to its slit-shaped mesopores (20–50 $\text{\AA}$) and compatibility with KOH ions ($\sim 3.6 \text{ \AA}$), enabling surface-dominated charge storage without requiring long-range ion diffusion. Conversely, ACNagKOH's poor performance (25 F/g, 72.1 Ωcm^2) aligns with its ink-bottle pore geometry ($\sim 18 \text{ \AA}$), which restricts electrolyte access. ACNagKOH's intermediate capacitance (32 F/g) and low ESR (15.1 Ωcm^2) reflect its hierarchical slit-shaped pores (592 m^2/g , $\sim 38 \text{ \AA}$), balancing surface area and ion percolation, even if dynamics remain unresolved. BET and TGA-FTIR-MS data corroborate these trends: ACNag's higher pore volume (0.55 cm^3/g) and retained hydration layers (4 % H_2O at 102 $^\circ\text{C}$) enhance electrolyte stability, while rGOag's limited surface area (20 m^2/g) and ChCIEG incompatibility (624.8 Ωcm^2) exacerbate performance losses. These results underscore that electrochemical efficiency in porous carbons can arise from static surface interactions or confined ion adsorption, decoupled from detectable diffusive motions, emphasizing the critical interplay between pore architecture, electrolyte chemistry, and charge storage mechanisms. The integrated analysis reveals a stark decoupling between detectable diffusive dynamics (QENS) and electrochemical performance.

3.6.1. Ion dynamics and storage mechanism

The QENS data provides dynamic evidence that supports the hybrid charge storage mechanism proposed in Section 3.5. The measurable ion diffusion ($D_t \sim 10^{-9} \text{ m}^2/\text{s}$) in ACNagKOH suggests a mechanism where ion transport plays an active role, compatible with both EDLC and pseudocapacitance requiring ion arrival at redox sites. In contrast, the absence of a resolvable quasi-elastic signal in ACNagChCIEG and rGOagKOH, despite their high electrochemical performance, indicates that charge storage in these systems may be dominated by highly localized or surface adsorption processes (pseudocapacitance) that do not involve long-range diffusion detectable within the spectrometer's time window. This decouples bulk ion mobility from capacitive performance in optimized porous architectures, where surface accessibility is

key [74].

3.7. Final analysis

The integrated analysis of electrochemical performance, pore structure, thermal stability, ion dynamics, and charge storage mechanisms reveals a clear structure-performance relationship in the studied materials. Table 5 provides an overview of the characterizations of the materials under study. The QENS data revealed a direct correlation between pore geometry, electrolyte compatibility, and ion dynamics. ACMagKOH and ACMagDry exhibited resolvable diffusion ($D_t \sim 10^{-9} \text{ m}^2/\text{s}$), consistent with ink-bottle micropores ($\sim 18 \text{ \AA}$) enabling limited but detectable water mobility. In contrast, ACNagChClEG's hierarchical slit-shaped pores ($\sim 38 \text{ \AA}$) achieved the highest capacitance (34 F/g) and low ESR ($15.6 \text{ } \Omega \text{ cm}^2$) despite unresolved HWHM, suggesting surface-dominated charge storage decoupled from long-range diffusion. Remarkably, rGOagKOH exceptional capacitance (68 F/g) with negligible QE signals highlights efficient electrostatic adsorption in stacked mesopores (20–50 $\text{\AA}$), bypassing diffusion-limited mechanisms. Conversely, rGOagChClEG poor performance (8 F/g, $625 \text{ } \Omega \text{ cm}^2$) reflects incompatibility with larger ChClEG ions and pore blockage, exacerbated by extreme CO_2 release (70 % at 555°C). TGA-FTIR-MS data further validate structural stability trends: ACNag retained hydration layers (4 % H_2O at 102°C) enhance electrolyte accessibility, while ACMag ink-bottle pores trap volatiles, increasing ESR. These results underscore that electrochemical efficiency in porous carbons is governed by a complex interplay of pore architecture, electrolyte chemistry, and ion confinement, where capacitive performance may arise from either dynamic diffusion or static surface interactions, depending on structural constraints.

4. Conclusions

This comprehensive study systematically investigated the electrochemical performance of ACMag, ACNag, and rGOag electrodes in both aqueous (KOH) and viscous eutectic (ChClEG) electrolytes, revealing stark differences in capacitance and equivalent series resistance (ESR). ACNag exhibited superior performance (34 F/g, $15.6 \text{ } \Omega \text{ cm}^2$) due to its

hierarchical slit-shaped mesopores, while ACMag suffered from ion-trapping in ink-bottle pores (25 F/g in KOH, 17 F/g in ChClEG), and rGOag showed extreme electrolyte dependence—excelling in KOH (68 F/g) but failing in ChClEG (8 F/g, $624.8 \text{ } \Omega \text{ cm}^2$). These disparities necessitated a deeper structural and chemical analysis to elucidate the underlying mechanisms governing ion transport and charge storage.

To resolve these performance variations, we conducted a multi-technique characterization of the powdered precursors (ACMp, ACNp, rGOp), beginning with BET surface area and pore size distribution analysis. ACNp's high surface area ($592.65 \text{ m}^2/\text{g}$) and hierarchical porosity ($0.573 \text{ cm}^3/\text{g}$ total pore volume) facilitated unrestricted ion diffusion, whereas ACMp's ink-bottle mesopores ($410.72 \text{ m}^2/\text{g}$, $0.384 \text{ cm}^3/\text{g}$) hindered electrolyte penetration. rGOp's ultra-low porosity ($20.13 \text{ m}^2/\text{g}$, $0.010 \text{ cm}^3/\text{g}$) explained its reliance on surface-driven pseudocapacitance and poor performance in viscous electrolytes. SEM and gas sorption hysteresis (Type IV isotherms, H3/H4) further confirmed these structural differences, directly correlating with electrochemical behavior.

Simultaneous TG-FTIR-MS analysis of the powders revealed that residual moisture, volatiles, and binder interactions critically influence electrode stability. ACNp's slit pores retained adsorbed water without impeding ion mobility, while ACMp's ink-bottle morphology trapped volatiles, increasing ESR. rGOp's agglomerated structure exacerbated PTFE-induced pore blockage, particularly in ChClEG. These findings underscore the necessity of pre-treating carbon materials—through thermal annealing or controlled activation—to remove synthesis residues and optimize pore accessibility before electrode fabrication.

Quasi-elastic neutron scattering (QENS) provided dynamic insights into ion mobility, showing resolvable diffusion in ACMagKOH ($\sim 10^{-9} \text{ m}^2/\text{s}$) but static surface interactions in ACNagChClEG. This dichotomy highlights that capacitive mechanisms vary with pore confinement: bulk diffusion dominates in accessible mesopores, while surface adsorption prevails in restricted geometries. The absence of detectable diffusion in rGOagChClEG further confirms that inadequate porosity leads to catastrophic kinetic limitations in viscous electrolytes.

These results establish a critical framework for supercapacitor development: (1) Precursor materials must be rigorously characterized (BET, SEM, thermal analysis) to ensure optimal porosity and purity

Table 5

Characterization techniques used for each type of sample used in this study and their respective most relevant results.

For Powder samples	BET Surface Area (m^2/g)	TGA-FTIR-MS Key Observations	Sample Electrode/ electrolyte	QENS Results	Specific Capacitance (F/g)	ESR ($\Omega \text{ cm}^2$)
ACMp	410.7 ± 7.3	H_2O loss peaks at 37°C (96.4 %), 119°C (3 %); CO_2 release at 355°C (4 %) Enhanced H_2O retention (119°C); CO_2/CO release above 355°C Higher volatile organics (1.5 % at 37°C); limited H_2O stability	ACMagDry	Resolved HWHM $D_t = 1.14 \times 10^{-9} \text{ m}^2/\text{s}$	N/A (Dry)	N/A (Dry)
			ACMagKOH	Resolved HWHM $D_t = 1.24 \times 10^{-9} \text{ m}^2/\text{s}$	25 ± 1.25	72.1 ± 0.44
			ACMagChClEG	Unresolved HWHM ($<0.054 \text{ meV}$)	17 ± 0.85	87.0 ± 0.36
ACNp	592.6 ± 8.0	Stabilized H_2O (4 % at 102°C); minimal CO_2/CO release High CO_2 release (3 % at 600°C); retained oxygen groups (C=O, C-O)	ACNagDry	No QE signal (delta-only fit)	N/A (Dry)	N/A (Dry)
			ACNagKOH	No QE signal (delta-only fit)	32 ± 1.6	15.1 ± 0.15
			ACNagChClEG	Unresolved HWHM ($<0.054 \text{ meV}$)	34 ± 1.7	15.6 ± 7.55
rGOp	20.1 ± 1.2	Minimal H_2O (5 % at 48°C); dominant CO_2 release (70 % at 555°C) Low H_2O retention; high CO_2/CO at 555°C (15–5 %) Extreme CO_2 release (70 % at 555°C); negligible H_2O /organics	rGOagDry	No QE signal (delta-only fit)	N/A (Dry)	N/A (Dry)
			rGOagKOH	No QE signal (delta-only fit)	68 ± 3.4	21.7 ± 0.92
			rGOagChClEG	Unresolved HWHM ($<0.054 \text{ meV}$)	8 ± 0.4	624.8 ± 71.4

before electrode fabrication. (2) Pore hierarchy must be tailored to electrolyte ion sizes, favoring slit-shaped mesopores for balanced accessibility and confinement. (3) Binder distribution and thermal treatments should minimize pore occlusion while enhancing electrode stability. (4) Advanced techniques like QENS and operando spectroscopy are indispensable for probing ion dynamics in complex architectures. Future work should integrate machine learning-guided pore design and sustainable manufacturing to bridge lab-scale innovations with industrial-scale supercapacitor production. (5) Future studies aiming for a deeper understanding of the surface chemistry could benefit from a rigorous X-ray Photoelectron Spectroscopy (XPS) analysis, provided it is conducted with the specialized peak-fitting protocols required for carbon materials to reliably quantify functional groups at the electrode-electrolyte interface. Furthermore, the application of Raman spectroscopy, and advanced correlative techniques such as in situ electrochemical Raman, would be highly beneficial to quantitatively link structural disorder and defect density with charge storage mechanisms and performance.

CRedit authorship contribution statement

Fernando Gabriel Benítez Jara: Writing – review & editing, Writing – original draft, Visualization, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jorge David Barrios Lémus:** Resources, Methodology, Data curation. **Jan Peter Embs:** Writing – review & editing, Visualization, Software, Formal analysis, Data curation. **Heloisa Nunes Bordallo:** Writing – review & editing, Validation, Supervision, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Rubens Nunes Faria:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Heloisa Nunes Bordallo reports financial support and equipment, drugs, or supplies were provided by Carlsberg Foundation (Grants CF21-0308, 2013_01_0589, CF14-0230, CF19-0521). Heloisa Nunes Bordallo reports financial support, equipment, drugs, or supplies, and travel were provided by Danish Agency for Science, Technology, and Innovation DANSCATT. Fernando Gabriel Benítez Jara reports financial support and travel were provided by National Scholarship Program Don Carlos Antonio López - BECAL of the Ministry of Finance, Government of the Republic of Paraguay. Fernando Gabriel Benítez Jara reports equipment, drugs, or supplies was provided by Carlsberg Foundation (Grants CF21-0308, 2013_01_0589, CF14-0230, CF19-0521). Fernando Gabriel Benítez Jara reports equipment, drugs, or supplies and travel were provided by Danish Agency for Science, Technology, and Innovation DANSCATT. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2025.238941>.

Data availability

Data will be made available on request.

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